

Effect of the Wyckoff position of K atom on the crystal structure and electronic properties of KFe_2Se_2 compound

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By the first-principle electronic structure calculations, we study the effect of Wyckoff position of K atom on the crystal and electronic structures of KFe_2Se_2 compound. When the K atoms take up the Wyckoff position *2a*, *2b* or *4c* (the related structure is called as Struc-2a, Struc-2b or Struc-4c), the calculated lattice constant *c* is in the range of 13.5~14.5 Å, 15.5~16.7 Å or 18.6~19.1 Å. Three concentric cylinder-like Fermi surfaces emerge around Γ -Z in Brillouin Zone for the Struc-2b in nonmagnetic state, different from the Struc-2a and Struc-4c. The Fe-Se-Fe angle is 107.8°, 108.8° or 110.7° in the collinear anti-ferromagnetic state and the superexchange interaction J_2 between two next neighbor Fe moments is 13.08 meV/S², 20.75 meV/S² or 11.86 meV/S² in Struc-2a, Struc-2b or Struc-4c structure respectively. The Struc-2b and Struc-4c have a good correspondence to the newly discovered superconducting phases with $T_c=40$ K and $T_c=30$ K in KFe_2Se_2 . Our findings provide a reasonable approach to understand the existence of multiple superconducting phases in alkali metal intercalated FeSe superconductor.

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INTRODUCTION

The recent observation of superconductivity about 30 K in the layered iron selenides compound $\text{K}_{0.8}\text{Fe}_2\text{Se}_2$ [1] initiated extensive research on the iron selenide superconductors, which was formed by intercalating alkali metal between FeSe layers and had the ThCr_2Si_2 -type structure (Fig. 1(a)). In contrast to the iron arsenide superconductors, $\text{A}_y\text{Fe}_{2-x}\text{Se}_2$ ($\text{A} = \text{K, Rb, Cs or Tl}$) is a new class of iron based superconductor. Their electronic structures are very different from those in the iron arsenide compounds, that is, only electron Fermi surfaces are presented around the zone corners while no hole Fermi surface near the zone center, which is confirmed by the experimental measurement [2] and the previous first principle calculations [3].

The crystal structures of $\text{A}_y\text{Fe}_{2-x}\text{Se}_2$ are complex since for different *x* values there are different Fe vacancy arrangement schemes. The X-rays, transmission electron microscopy, and neutron scattering measurements indicate that the composition of K-intercalated FeSe superconductors was close to $\text{K}_y\text{Fe}_{1.6}\text{Se}_2$ with a fivefold expansion of the parent ThCr_2Si_2 unit cell in the *ab* plane, namely a $\sqrt{5} \times \sqrt{5}$ Fe-vacancies superstructure [4, 5]. Another experiment show that there exists a rhombus Fe vacancy pattern related to $\text{K}_y\text{Fe}_{1.5}\text{Se}_2$ [6]. However it is reported that in the same sample there exist two distinct phases, the insulating phase with well-defined $\sqrt{5} \times \sqrt{5}$ Fe-vacancies superstructure and another KFe_2Se_2 phase containing no Fe vacancies, the latter being suggested to be responsible for superconductivity [7]. The composition and structure responsible for the superconductivity is still in debate.

Most recently, Li, Na, Ca, Ba, Yb, or Eu layer is in-

serted between adjacent FeSe layers to optimize the superconducting properties of the iron selenides compounds [8]. It is the surprising phenomenon that two superconducting phases were observed in $\text{K}_{0.8}\text{Fe}_2\text{Se}_2$ with the one T_c of 30 K and another T_c of 40 K. In addition, two kinds of crystal unit cell with unexpectedly long lattice constant $c=16.14$ Å and $c=20.48$ Å were found to correspond to two superconducting phases, and the $c=20.48$ Å unit cell disappeared after one hour's exposure to air accompanying the T_c change from 40 K to 30 K. In the other reports, two superconducting phases were ever observed in $\text{K}_x\text{Fe}_{2-y}\text{Se}_2$ [9–11]. However, there are rare theoretical studies on the difference of crystal and electronic structures between these superconducting phases, and the reason for higher T_c in new superconducting phase.

The Wyckoff position of K atoms has a great influence on *c* axis length of crystal unit cell and the Fermi surface characters in KFe_2Se_2 . In experiment the occupations of different Wyckoff positions by alkali metal atoms are observed [12]. Meanwhile, the fact that no clear peak due to N-H vibrations is detected in infrared spectroscopy measurements [8] excludes the existence of NH_3 in KFe_2Se_2 synthesized by the liquid ammonia method. So we can deduce that three superconducting phases of KFe_2Se_2 with different lattice parameter *c* should correspond to the different Wyckoff position occupied by K atoms. In the paper, we focus on the effect of different Wyckoff position of K atom in space group $I4/mmm$ on the crystal structure and electronic properties of KFe_2Se_2 , with K atom sited in *2a*, *2b* or *4c* Wyckoff position respectively. The paper was organized as follows. Firstly, we optimize the crystal structure and obtain the reasonable lattice constants of KFe_2Se_2 , in agreement with the experimen-

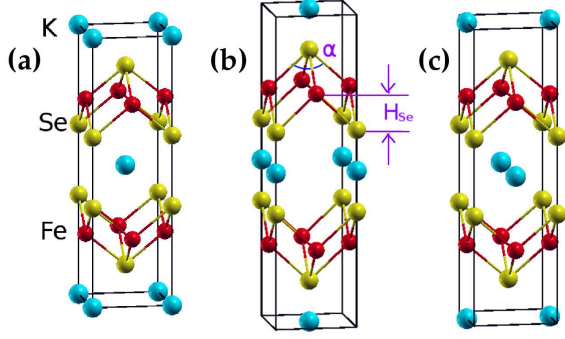


FIG. 1: (Color online) Schematic structure of the tetragonal unit cell of $K_xFe_2Se_2$ containing two formula units: (a) K atom is situated in $2a$ Wyckoff position, (b) K atom is situated in $2b$ Wyckoff position, (c) K atom is situated in $4c$ Wyckoff position and only two of four $4c$ positions are occupied, the α and H_{Se} indicate the Fe-Se-Fe bond angle and the Se height to Fe plane.

tal values of $c=14.04$ Å, $c=16.16$ Å, and $c=20.48$ Å in three superconducting phases. Secondly, the electronic structures of Struc-4c is similar to those of Struc-2a implying they have the similar superconducting behavior. The Fermi surface of Struc-2b exhibits the different characters, that is, the concentric cylinder like Fermi surfaces are presented around Γ -Z, which should have a necessary connection to the superconductivity with the higher $T_c=40$ K. Lastly, from three aspects of the Fe-Se-Fe angle, electronic structures and the next neighbor superexchange interaction J_2 , we demonstrate that the Struc-2b structure is closely related to the superconducting phase with $T_c=40$ K, while Struc-4c to the superconducting phase with $T_c=30$ K in KFe_2Se_2 synthesized by the ammonothermal method.

METHOD AND DETAILS

In our calculations the plane wave basis method was used [13]. We adopted the generalized gradient approximation (GGA) with Perdew-Burke-Ernzerhof formula [14] for the exchange-correlation potentials. The ultrasoft pseudopotentials [15] were used to model the electron-ion interactions. After the full convergency test, the kinetic energy cut-off and the charge density cut-off of the plane wave basis were chosen to be 800 eV and 6400 eV, respectively. The Gaussian broadening technique was used and a mesh of $16 \times 16 \times 12$ k-points were sampled for the Brillouin-zone integration. In the calculations, the lattice parameters with the internal atomic coordinates were optimized by the energy minimization. The Struc-4c tetragonal unit cell should have included four K atoms, but only two K atoms is included in order to keep the same composition K:Fe:Se=1:2:2 for Struc-2a, Struc-2b and Struc-4c.

RESULTS AND DISCUSSION

For the first part, we study the structural properties of KFe_2Se_2 including the lattice parameter, the Se height to Fe plane H_{Se} and the Fe-Se-Fe bond angle α in FeSe layer. Alkali metal intercalated iron selenides have the tetragonal crystal structure with the space group $I4/mmm$. Fe atom and Se atom are sited in the $4d$ and $4e$ Wyckoff position in this space group respectively, constructing the stable FeSe layer in KFe_2Se_2 compound. In the previous studies KFe_2Se_2 is thought to have the $ThCr_2Si_2$ -type structure and K atom is located at the $2a$ Wyckoff position similar to Ba atom in $BaFe_2As_2$, shown in Fig. 1(a). The $2a$ position is at the body center of the Se tetragonal formed by eight Se atoms between two neighbor Fe layers, while the $2b$ and $4c$ positions are at the middle point of the side edge and the center of side face in the Se tetragonal body, see Fig. 1(b) and (c).

We perform the structure optimizations of KFe_2Se_2 in which the K atoms is sited in $2a$, $2b$ and $4c$ Wyckoff position in space group $I4/mmm$ respectively. The calculated results are showed in the Table. I and the optimized lattice parameters c are compared with the measured ones.

TABLE I: The lattice parameters c , the Fe-Se-Fe bond angle α and the Se height H_{Se} to Fe plane of KFe_2Se_2 in several magnetic orderings for the Struc-2a, Struc-2b and Struc-4c phases. In Bicoll-AFM order the lattice constants a shrinking lead to the decrease of α along the FM direction and the distortion of Fe layer lead to the fluctuation of H_{Se} , shown in bracket. For the Struc-2b the Bicoll-AFM state is not stable.

structure	magnetic phase	$c(\text{\AA})$	$H_{Se}(\text{\AA})$	$\alpha(^{\circ})$
Struc-2a	Nonmag	13.30	1.29	112.3
	FM	14.04	1.62	98.7
	Neel-AFM	13.67	1.37	109.5
	Coll-AFM	13.79	1.42	107.8
	Bicoll-AFM	14.45	1.45	107.0
			(1.64)	(97.2)
Exper.[1]		14.04		
Struc-2b	Nonmag	18.60	1.31	110.6
	FM	19.04	1.59	99.5
	Neel-AFM	18.97	1.39	108.1
	Coll-AFM	18.84	1.40	108.8
	Bicoll-AFM	—	—	—
Exper.[8]		20.48		
Struc-4c	Nonmag	15.46	1.30	113.9
	FM	16.70	1.57	102.1
	Neel-AFM	15.75	1.35	111.2
	Coll-AFM	15.79	1.38	110.7
	Bicoll-AFM	16.24	1.42	109.2
			(1.64)	(96.7)
Exper.[8]		16.16		

When K atom take up the $2a$ position, the relaxed lattice constant c is about $13.3 \sim 14.5$ Å for different magnetic phases, consistent with the measured data 14.04 Å synthesized by high-temperature routes. In the case of K occupying the $2b$ and $4c$ position, the optimized parameters c are about $18.6 \sim 19.0$ Å and $15.5 \sim 16.7$ Å respectively for different magnetic orderings, with good agreement with the observed lattice c 20.48 Å and 16.16 Å synthesized using the ammonothermal method.

The T_c dependence of the As height to Fe plane and the Fe-As-Fe angle have been investigated extensively in iron arsenide superconductor and the neutron diffraction measurements reveal that T_c becomes maximum when the Fe-As-Fe angle is close to 109.4° , corresponding to the perfect FeAs_4 tetrahedron [16]. The calculated Se heights to Fe plane H_{Se} and the Fe-As-Fe angles α in three structure phases of KFe_2Se_2 are presented in Table. I. In general, the Se heights within the given anti-ferromagnetic orders for three structure phases are in the range of $1.35 \sim 1.45$ Å and the discrepancy of Fe-As-Fe angle between our calculation and the ideal value 109.4° is less than 2.4° (except the angles along ferromagnetic direction of Bicoll-AFM order in Struc-2a and Struc-4c). Since the Coll-AFM magnetic phase is the lowest or second lowest energy state for three structure phases of KFe_2Se_2 (see Table.II), it is convenient for us to compare the Fe-Se-Fe angles α in KFe_2Se_2 in this magnetic order. In our calculations the angles in Struc-2a, Struc-2b and Struc-4c phases are 107.0° , 108.8° , and 110.7° . Among three structures, the 108.8° in Struc-2b is the most close to 109.4° . According to the qualitative conclusion that the ideal tetrahedral FeAs_4 or FeSe_4 correspond to the maximum of T_c , we suggest that Struc-2b is related to the $T_c=40$ K, while Struc-2a and Struc-4c correspond to T_c about 30 K superconducting phases. As for the Se height to Fe plane, it is dependent on both the Fe-Se-Fe angle and the crystal lattice constants a (or b), there is no definite correlation between Se height and T_c .

For the second part, we investigate the electronic properties of the Struc-2a, Struc-2b and Struc-4c structures in nonmagnetic state. Fig. 2 (a), (b) and (c) show the total and orbital resolved partial density of states (DOS) for three structures respectively. The DOS ranging from -7 to -3 eV are formed by the hybridization between Se 4p and Fe 3d orbitals. The DOS at Fermi level is mainly from Fe 3d orbital and a small contribution is from Se 4p orbital. The Struc-2b has the maximum 3.37 states/eV per unit cell, compared with 2.15 of Struc-2a and 2.43 of Struc-2c, which reveal that Struc-2b should be possessed of some especial electronic properties different from the Struc-2a and Struc-4c phase.

Fig.3 (a), (d) and (c), (f) show the band structures and Fermi surfaces of the Struc-2a and Struc-4c phase respectively. The two structure phases have a great resemblance in the band structure and the topological character of Fermi surface, including that two Fermi surface

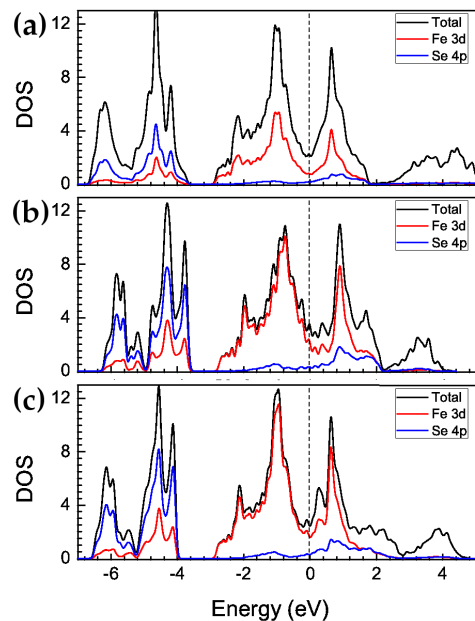


FIG. 2: (Color online) Total and orbital-resolved partial density of states per primitive cell of KFe_2Se_2 for the Struc-2a, Struc-2b and Struc-4c structures. The Fermi level is set to zero.

sheets at the Brillouin Zone corner and a Fermi surface pocket around Z point. They also share the critical feature that no Fermi surface appear near Γ point obviously different from the iron arsenide superconductor. According to this resemblance, the Struc-2a and Struc-4c structure should have the similar superconducting behaviors and the T_c should be approximate to each other, associated with the facts that T_c are about 30 K in both the $c=16.16$ Å and the $c=14.04$ Å superconducting phases in KFe_2Se_2 compound.

From Fig.3 (b), (e) we can see that there are three bands crossing the Fermi level for the Struc-2b and the Fermi surfaces present better 2-dimensionality characters than that of Struc-2a phase. The most surprising thing is that there exist three cylinder shape Fermi surfaces centered around Γ -Z, the innermost is hole-type derived from the band 1 marked in Fig.3 (b) and the other two is electron-type derived from the energy band 2. The concentric cylinder Fermi surface sheets along Γ -Z is the typical features in iron arsenide superconductor, so the electronic structure of the Struc-2b phase of KFe_2Se_2 is very similar to the electronic structure of iron arsenide superconductor such as LaFeAsO and BaFe_2As_2 . In Struc-2b phase, it is the emergence of cylinder Fermi surface around Γ -Z that is expected to bring about the stronger superconducting electron pairing than that in the Struc-2a and Struc-4c phases. The experimental $T_c=40$ K superconducting phase should correspond to the Struc-2b phase in KFe_2Se_2 compound.

For the third part, we discuss the magnetic interaction

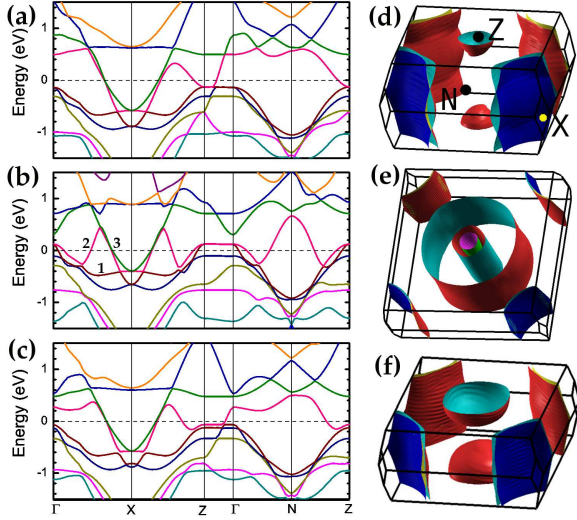


FIG. 3: (Color online) The energy band structures of KFe_2Se_2 for the Struc-2a, Struc-2b and Struc-4c structure phase shown in (a), (b) and (c), and the corresponding Fermi surfaces shown in (d), (e) and (f) respectively. The bands crossing the Fermi energy denoted by line 1, 2 and 3 in (b). The Fermi level is set to zero.

between Fe moments and its connection to the superconducting temperature T_c . The magnetic moments around each Fe atom were found to be about $2.8 \mu_B$ in the alkali metal intercalated iron selenide superconductors [5], much larger than the moments in the iron arsenide superconducting materials, so the magnetic interactions among Fe atoms play an important role in determination of structural and electronic properties of AFe_2Se_2 ($\text{A}=\text{K}, \text{Rb}, \text{Cs}$ and Tl). We perform the calculation for the Struc-2a, Struc-2b and Struc-4c structures under the nonmagnetic order (NM), ferromagnetic order (FM), checkerboard antiferromagnetic order (Neel-AFM), collinear antiferromagnetic order (Coll-AFM), and bi-collinear antiferromagnetic order (Bicoll-AFM). The magnetic ground states for the Struc-2a and Struc-4c are the Bicoll-AFM order. The lowest energy state for the Struc-2b is the Coll-AFM order, since under the Bicoll-AFM order K atoms will migrate to 4c position and lead to the Struc-4c structure in our calculations. The energies of three structures under several magnetic orders relative to the nonmagnetic energy of the Struc-2a are listed in the Table. II.

To qualify the magnetic interactions, we can assume that the energy differences among these magnetic orders mainly originate from the interactions between each two Fe moments with spin \vec{S} . Then the frustrated Heisenberg model with the nearest, next nearest and third next nearest neighbor couplings J_1 , J_2 and J_3 can be used to describe the interactions in KFe_2Se_2 system, namely,

$$H = J_1 \sum_{\langle ij \rangle} \vec{S}_i \cdot \vec{S}_j + J_2 \sum_{\langle\langle ij \rangle\rangle} \vec{S}_i \cdot \vec{S}_j + J_3 \sum_{\langle\langle\langle ij \rangle\rangle\rangle} \vec{S}_i \cdot \vec{S}_j, \quad (1)$$

whereas $\langle ij \rangle$, $\langle\langle ij \rangle\rangle$ and $\langle\langle\langle ij \rangle\rangle\rangle$ denote the summation over the nearest, next-nearest, and next-next-nearest neighbors, respectively. From the energy data in Table. II, the superexchange coupling parameters J_1 and J_2 are shown in the rightmost column in Table. II (The detailed calculation is referred to Appendix of Ref. 17).

By comparing these exchange coupling values, we notice that the Struc-2a and Struc-4c phases have the similar features in the magnetic interactions, but the Struc-2b phase is somewhat different from them. Here we should pay close attention to the next neighbor superexchange interaction J_2 in three structures. Theoretically, the two band model $t - J_1 - J_2$ indicates that the T_c in iron based superconductor is proportional to the J_2 [18] and we also have drawn the same conclusion in the previous first principles studies on the iron based materials [19, 20]. From this point of view, we can obtain the results that Struc-2b phase has the higher superconducting transition temperature T_c than Struc-2a and Struc-4c, and the latter two structures have the similar T_c values, because the next neighbor superexchange interaction $J_2 = 20.74 \text{ meV}/S^2$ in Struc-2b is larger than $J_2 = 13.08 \text{ meV}/S^2$ in Struc-2a and $J_2 = 11.86 \text{ meV}/S^2$ in Struc-4c. The opinion that the higher T_c superconducting phase occur in the Struc-2b structure is consistent with our analysis about both the Fermi surface features and the Fe-Se-Fe angle. The consistency is easy to understand because the superexchange interaction J_2 between two next nearest neighbor Fe atoms is bridged by Se atom and has a direct connec-

TABLE II: The energy per Fe atom, magnetic moment around Fe atom and the nearest and next nearest neighbor superexchange coupling of KFe_2Se_2 system in different magnetic orderings for the Struc-2a, Struc-2b and Struc-4c structures. The nonmagnetic energy of Struc-2a is set to zero. For Struc-2b, the Bicoll-AFM state is not stable.

structure	magnetic phase	Energy (meV/Fe)	moment (μ_B)	J_1, J_2 (meV/ S^2)
Struc-2a	Nonmag	0.0	0	
	FM	-205.48	3.20	$J_1 = -25.27$
	Neel-AFM	-104.42	2.25	$J_2 = 13.08$
	Coll-AFM	-207.41	2.75	
Struc-2b	Bicoll-AFM	-248.25	2.75	
	Nonmag	512.97	0	
	FM	388.02	3.10	$J_1 = 2.79$
	Neel-AFM	376.85	2.36	$J_2 = 20.75$
	Coll-AFM	298.32	2.85	
Struc-4c	Bicoll-AFM	—	—	
	Nonmag	307.83	0.0	
	FM	77.39	3.16	$J_1 = -24.48$
	Neel-AFM	175.31	2.37	$J_2 = 11.86$
	Coll-AFM	78.90	2.79	
	Bicoll-AFM	30.77	2.79	

tion to the Fe-Se-Fe angle.

In addition, we do some discussion about the issue why K atom can locate in $2b$ or $4c$ Wyckoff position. Fixed the lattice parameters to the experimental values, we optimize the K positions with initial K position sited in the $2a$, $2b$ or $4c$ respectively. The K positions do not change from the initial $2a$ or $4c$ to $2b$ position with the fixed c axis at 20.48 Å, or from the initial $2a$ or $2b$ to $4c$ with the fixed c axis at 16.16 Å. These calculations indicate that the Struc-2b and Struc-4c are the metastable structure phases relative to the Struc-2a. As to the formation of these metastable phases, we can assume the process happened as blow. At first, the NH₃ molecules and K atoms enter in between FeSe layers together and K atoms sit in $2b$ or $4c$ Wyckoff positions, leading to the large length of lattice c . Then, NH₃ escape from the compounds and K atoms still sit in $2b$ or $4c$ position. We also investigate the energy change with the lattice parameter c increasing for the Struc-2a, Struc-2b and Struc-4c respectively. When the length of lattice parameter c is large than 18.58 Å, the energy of the Struc-4c begin to become less than the one of Struc-2a phase. When the parameter c is larger than 20.85 Å, the Struc-2b energy is the lowest one among three structure phases. The results mean that with the large lattice parameter c the K atom prefers to occupy the $4c$ or $2b$ Wyckoff position.

In summary, we have investigated the effect of different Wyckoff position of K atom on the crystal structure of KFe₂Se₂ by the first principle calculations. We conclude that the occupations of Wyckoff position $2b$ and $4c$ by K atom correspond to the $T_c=40$ K and $T_c=30$ K superconducting phases in experiment respectively, which are demonstrated by the calculated lattice parameters, Fe-Se-Fe angle, electronic structures and superexchange coupling J_2 . Our results have a good agreement with the experiment and provide a reasonable approach to understand the new superconducting phases in KFe₂Se₂.

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